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CATALYTIC CONJUGATION OF LINSEED AND SOYBEAN OILS

by

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CATALYTIC CONJUGATION OF LINSEED AND SOYBEAN OILS

I. INTRODUCTION

For a number of years, it has been recognized that the superior drying properties of tung oil are due to the presence of conjugated isomers of linolenic acid. In the hope of securing similar drying properties in linseed and soybean oils, attempts were made to convert the linoleic and linolenic acids occurring in combination in these oils into their conjugated isomers. Successful isomerization was achieved by treating the oils with alkali at high temperatures and pressures, either in alcoholic solution (1) or in aqueous solution (2).

The alkali conjugation processes, however, cause saponification of the glyceride. While this circumstance may not be disadvantageous to the user of free fat acids, the necessity of re-esterifying in order to produce an oil for use in paint and varnish occasions considerable added expense. Furthermore, satisfactory color, viscosity, and other properties are difficult to obtain.

One approach to the problem is neutral catalytic isomerization of the whole glyceride, that is, isomerization or conjugation is induced by bringing the oil into contact with a suitable neutral catalyst under appropriate conditions which preclude splitting of the glyceride.

The object of this report is to disclose the details of a successful method for neutral catalytic isomerization. In addition to descriptions of catalyst and procedure, evaluative data for the finished oils will be presented.

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(1) Bradley, T. F., U. S. Patent 2,350,583, June 6, 1944.
(2) Burr, G. O., U. S. Patent 2,242,230, May 20, 1941.

II. THE PROCESS

The process to be described consists essentially of bringing a vegetable oil in contact with an activated nickel-carbon catalyst at temperatures between 160°-200° C. in an inert atmosphere. In this way, oils are produced which contain 25-35 percent conjugation, and which have low acid numbers, viscosities, and color indices. The glyceride linkages are not disturbed, nor is additional chemical treatment required. In Table 2.1 are presented properties of typical oils produced by neutral catalytic conjugation. The process may be applied also to other neutral derivatives of linoleic and linolenic acids, such as, monohydric alcohol esters and alcohols.

Conjugation is best measured by means of the ultraviolet absorption using a Beckman spectrophotometer (1). However, after a number of determinations on soybean and linseed oils, it is possible to construct graphs which permit approximate estimation of conjugation from the refractive index, provided that excessive polymerization has not occurred. A viscosity of D (Gardner) in the isomerized oil may be taken as the upper limit for application of this method. Typical graphs are shown in Figures 2 and 3. The average accuracy to be expected is approximately ±2 units of percent conjugation, although most of the time, values within ±1 unit of the spectrophotometric result are obtained. Infrequently, values obtained spectrophotometrically deviate widely from the values determined graphically. No satisfactory explanation for this deviation has been suggested.

The exact location (against the coordinates) of the curves in these graphs depends on the initial refractive index of the oil. Within the natural variation in refractive index among samples, the curve may be shifted against the coordinates without significantly affecting the results.

The diene number may also be used to estimate the percent of conjugation, although it is not as convenient as the methods just described. The iodine number method is not recommended.

The various steps in the process are shown diagrammatically in the Flow Sheet, and they will be discussed according to the following outline:

A. Preparation of catalyst compositions
B. Activation of catalyst
C. Selection of oil
D. Isomerization
E. Separation of oil and catalyst
F. Re-use of catalyst
G. Properties of oils
H. Recovery of nickel from spent catalysts

A. Preparation of Catalyst Compositions.- The catalyst consists of a deposit of reduced nickel (17-19 percent) on activated carbon black (83-81 percent). Both components, in intimate association, are needed, since either used alone, or mechanical mixtures thereof, produces relatively little conjugation (Table 2.2).

Four methods of preparing catalyst compositions have been developed. Each composition yields an active isomerization catalyst upon reduction with hydrogen at elevated temperatures.

Type A. Nickel formate is deposited on activated carbon.
Type B. Nickel chloride is deposited on activated carbon, and the mixture is treated with sodium bicarbonate.

Type C. Nickel nitrate is deposited on activated carbon, and the mixture is treated with ammonium carbonate.

Type D. Nickel nitrate is deposited on activated carbon.

The activated carbon black must be carefully selected, as not all types are suitable. In general, a carbon is needed which is characterized by high adsorptivity and large surface area, and which contains a minimum of inorganic impurities. The necessary properties of the carbon are only imperfectly understood; however, those experienced in the manufacture of activated carbon should be able to ascertain the methods of production and activation required to yield carbon black satisfactory for use in the catalyst.

After examination of a number of blacks of various grades, obtained from several manufacturers, Nuchars XXX and C-190 were found to give the best results (Table 2.3).

The nickel salts used in the process are a purified commercial grade. Typical analyses are as follows:

Nickel Nitrate

		Percent
Assay:	$Ni(NO_3)_2 \cdot 6H_2O$	99.2
	Ni	20.0
	Fe	0.01
	Cu	0.007
	Pb	0.01
	Zn	0.007
	Cl	0.007
	SO_4	0.007
	Ca+Mg+Na	0.25
	H_2O Insol.	0.05

Nickel Formate

		Percent
Assay:	$Ni(HCO_2)_2 \cdot 2H_2O$	96.0
	Ni	30.5
	Cl	0.08
	Fe	0.03
	SO_4	0.12
	H_2O Insol.	0.5

The four types of catalyst compositions described, and the activated catalysts produced from them, are designated A, B, C, and D. Typical laboratory procedures for their preparation follow. The moisture-free compositions are stable indefinitely.

Type A.- A filtered solution of 192 g. of nickel formate in 5 liters of distilled water heated to 90° C. is mixed with 210 g. of activated carbon, and water is then evaporated from the mixture until a paste is formed. A steam-heated gyratory mixer is satisfactory for this operation. The paste is finally dried 16 hours at 90°-100° C., ground to a fine powder, and stored in moistureproof containers.

Type B.- This composition is prepared from carbon, nickel chloride, and sodium bicarbonate in a manner analogous to that given for Type C. Its use is not recommended because it is very erratic in performance and unreliable for use in larger quantities (100-300 g.), although small amounts (20 g.) of very active catalysts are produced from it by reduction.

Type C.- A solution of 174 g. of nickel nitrate in 240 ml. of distilled water is mixed intimately with 150 g. of activated carbon, either with a sigma-bladed stainless steel mixer, or with a mortar and pestle. A solution of 102 g. of ammonium carbonate in 600 ml. of water is then added slowly with constant agitation. After effervescence ceases, the mixture is filtered, and the cake is washed twice with 200 ml. of water and dried 16 hours at 90°-100° C. The composition is finally powdered and stored in moistureproof containers. In general, catalysts prepared from this composition induce higher conjugation in soybean than in linseed oil.

Type D.- This catalyst is prepared in a manner similar to that for Type C with the omission of the addition of ammonium carbonate and of the washing operations. If a stainless steel mixer is used, it is advantageous to heat it with steam during mixing, in order to prevent the formation of pellets. The resulting damp powder is dried further by heating 16 hours at 90° C. Higher temperatures should be avoided, since these frequently cause the catalyst to ignite. After drying, the catalyst is powdered and stored in moistureproof containers.

No difficulties should arise in preparing larger amounts of catalyst composition. Conventional equipment for conducting mixing and drying operations should be satisfactory. Forced circulation of air during drying should be avoided in order to prevent combustion of the catalyst. The Type D catalyst should not be stored while still damp, for under these conditions, a slow spontaneous oxidation occurs with the liberation of nitrous fumes. Catalysts prepared from such oxidized compositions are relatively inactive.

B. Activation of Catalyst.- Active catalysts are prepared by reduction of catalyst composition at 360° ± 10° C. for 2 to 3 hours. Intimate contact with hydrogen is necessary. This can be accomplished by vigorous,

effective stirring or by other means. The activity of the final catalyst is affected by the length and temperature of activation. The influence of these factors is shown by the data of Table 2.4.

A satisfactory laboratory apparatus is shown in Figure 1. A 5-liter flask is used, permitting the reduction of about 300 g. of catalyst composition. This amount is sufficient for the isomerization of one gallon of oil. In the apparatus shown, contact of catalyst composition with hydrogen was accomplished by stirring the mixture with a Hershberg stirrer constructed of Nichrome wire (operated at 50-60 r.p.m.) and by passing hydrogen through the flask at the rate of 200 cc. per minute. Hydrogen is admitted only during the periods of heating up and holding at 360° C., cooling being conducted under an atmosphere of carbon dioxide. Single runs with the catalyst have indicated that aluminum, copper, zinc, mild steel, and rusty iron do not have a deleterious effect on the activity of catalyst prepared in their presence. These metals also appear not to affect the results if they are present during the subsequent isomerization.

Reduction proceeds smoothly except with Catalyst D. In this case, a violent exothermic decomposition occurs during the heating-up period at about 200° C., accompanied by copious evolution of nitrous fumes. In the apparatus just discussed, this gas is vented harmlessly through a large-bore outlet tube. It is believed that 300-325 g. may be the maximum amount of Catalyst D composition which can be decomposed safely in one batch. Large amounts may be handled by introducing slowly the powdered catalyst composition into a vessel maintained above the decomposition point. The decomposed composition is then heated to 360° C. and reduced as one batch.

An alternative procedure consists of decomposing the catalyst gradually under carbon dioxide and cooling. The decomposed catalyst is unaffected by air and may be activated by reduction with hydrogen as needed.

Following activation, the oil may be added to the catalyst, and isomerization may be conducted in the same vessel. If the active catalyst is to be stored or transferred, this may be accomplished by first covering the catalyst with oil. Activated catalyst is sensitive to air, although it is not obviously pyrophoric. One sample of activated catalyst, which would have been expected to induce about 33 percent conjugation in soybean oil, actually gave an oil containing 27 percent conjugation after stirring the catalyst in air at room temperature for 15 minutes.

A typical experiment was conducted as follows: In the flask, shown in Figure 1, was placed 312 g. of Catalyst D composition. Hydrogen was then introduced at the rate of 200 cc. per minute, after passage through a flowmeter, bubbler (soybean methyl esters are satisfactory for the bubbler fluid), and a cotton filter. The flask was then heated slowly to 200° C., without stirring, by means of the heating jacket. After decomposition of the catalyst, which required only a few seconds, the temperature was quickly raised to 360° C. by means of the jacket and hot

plate, and stirring was commenced. After 3 hours, the hydrogen flow was replaced by carbon dioxide, and the active catalyst was cooled to 100° C. One gallon of alkali-refined soybean oil was then added through the funnel and mixed thoroughly with the catalyst. The mixture may be stored for periods up to one week, transferred, or processed further. Storage for longer periods has not been tested.

This same procedure is followed with the other catalyst compositions, except that the composition may be heated immediately to 360° C.

C. Selection of Oil.- With any of the catalysts described, use of an alkali-refined soybean or linseed oil resulted in higher initial isomerization and greater retention of activity of the catalyst than when lower grades of oil were used. Table 2.5 contains specifications for the oils which have given the optimum results. It will not be necessary to discuss these specifications in detail except to point out that oils with somewhat higher acid numbers (0.6-0.7) have been used with equally good results. The color of soybean oil, if other factors are constant, may be as high as 11 (Gardner). With linseed oil, on the other hand, satisfactory isomerization was not obtained when the color exceeded that specified (see Table 2.6).

If it is not essential to retain catalyst activity, the specifications for soybean oil may be relaxed. For example, degummed or alcohol-extracted soybean oil gives excellent results, and nonbreak soybean oil gives fair results. Crude expeller oil develops about one-third the conjugation of the best oils. Results with various grades of oil are shown in Tables 2.6 and 2.9.

A special grade of degummed soybean oil containing 0.02 percent break and having an acid value of 1.0 and a color of 11 (Gardner) gave excellent results and permitted five uses of the catalyst for an average of 27 percent conjugation (Table 2.13).

D. Isomerization.- Isomerization is carried out by heating the activated catalyst and the desired oil in an inert atmosphere and with constant stirring. The proportion of oil to catalyst may be varied somewhat, but optimum results are obtained in the presence of 1-1/2 percent nickel and 5 percent carbon, based on the weight of oil (in the case of Catalyst D, this corresponds to 9 g. of catalyst composition per 100 g. of oil). In Table 1.7 are given some of the results obtained when various ratios of nickel-to-carbon are employed. If large amounts of a given catalyst are employed, isomerization occurs with great rapidity (Table 2.14).

Isomerization is obtained at temperatures between 160°-200° C. The rate of appearance of conjugation increases with temperature (Table 2.8).

At 160°-170° C., 6 hours is required for development of about 26-30 percent conjugation; at higher temperatures, the time may be reduced

substantially. In Figure 4, the development of conjugation during isomerization is shown graphically. It is necessary to control the temperature carefully as retention of activity (see Section F) and drying properties of the conjugated oil (see Section G of Part II, Part IV, and Table 4.1) depend on the temperature of isomerization.

Isomerization may be carried out satisfactorily in vessels of glass, stainless steel or aluminum, or in glass-lined equipment.

E. Separation of Oil and Catalyst.- Separation of the oil-catalyst mixture is difficult because the concentration of catalyst is high (6-9 percent), and because the filtering properties of the catalyst are substantially those of carbon black. Furthermore, the addition of filter aids affects the activity of the catalyst and reduces the amount of oil which can be isomerized by a given amount of catalyst.

Exploratory experiments were conducted on the filtration of catalyst-oil mixture in the absence of filter aids. A small Sperry plate-and-frame filter with 52-thread filter cloth and no precoat was used. After filtrations at several pressures, the data obtained were used in estimating filtration costs for the plate-and-frame filter, the pressure-leaf filter, and the continuous vacuum filter.

Upon the basis of 1,000 gallons of filtrate per day, the respective costs for these filters amount to 0.035, 0.042, and 0.053 cents per pound of filtrate. If 10,000 gallons a day were filtered, costs would be 0.021, 0.030, and 0.009 cents per pound of filtrate. These cost estimates include items such as labor, overhead, taxes, depreciation, maintenance, and amortization of equipment.

Of the three types of filters, the continuous vacuum filter should lend itself best to recovery of catalyst. Probably a precoat could be used with this filter since its doctor blade could be adjusted to prevent contamination of recovered catalysts with excessive amounts of filter aid.

Another type of filter which appears to be suitable for use with catalyst-oil mixtures is the spring filter. In this filter, filtration occurs through the interstices of a stretched spring. Filters of this type are readily cleaned, and the filter cake is easily recovered.

A satisfactory method of separation will require a careful balancing of technical and economic factors. Thus, the acceleration in filtering obtained with filter aids must be reconciled with loss of catalyst activity. Consideration must also be given to the saving in raw material costs obtainable by choice of a lower grade of oil, for example, degummed soybean oil. This saving might well neutralize the increased catalyst cost occasioned by shorter catalyst life. Furthermore, filter aids probably could be employed without further limitation of catalyst life when lower grades of oil are used.

F. Re-use of Catalyst.

1. Filter Aids Absent.- Any of the types of catalyst described may be used to conjugate more than one batch of oil without additional activation or treatment of any kind. The conditions to be met require: (1) that the oil meets the specifications of Table 2.5 (see Section C and also Tables 2.9, 2.10, and 2.13); (2) that the temperature of isomerization is at least 170° C.; and (3) that the catalyst is not exposed excessively to air during separation from the oil. It may be mentioned at this point that failure of a fresh catalyst to produce more than a certain amount of conjugation may be attributed to the probable existence of an equilibrium among nonconjugated and conjugated isomers rather than to deactivation.

Condition (3) is determined by the extent to which oil is removed from the filter cake during filtration. In general, it has been found that if the cake contains 50-60 percent by weight of oil, this oil coats the particles of catalyst and protects them from the action of air for a period of several hours.

The amount of fresh oil to be treated with a given weight of used catalyst is corrected for the oil content of the used catalyst and for losses of catalyst occurring during filtration. The losses must be determined through trial runs using a given method of filtration. The magnitude of the corrections may be judged from the data of Tables 2.9 and 2.10. The refractive index of oil obtained from the mixture of fresh oil and used catalyst furnishes a convenient check upon the degree of removal of oil from the used catalyst. Thus, if a refined soybean oil of refractive index 1.4718 is being used, the refractive index of the oil from the mixture should not be below 1.4723 upon the first re-use of catalyst.

The amount of conjugation obtained with used catalysts is always somewhat less than that obtained upon first use of the catalyst. Furthermore, the activity tends to decrease with each successive use, although the trend is not uniform but may include sudden increases and decreases of activity. Finally, the catalyst becomes dead. In some instances, a catalyst has been used as many as ten times before inactivity is reached. Usually, however, five uses may be obtained with an alkali-refined oil. If the catalyst becomes sluggish during re-use, the desired amount of conjugation may usually, but not infallibly, be obtained either by prolonging the time of isomerization, or by increasing the temperature (not above 175° C., however, if an oil of good drying properties is desired).

Since the amount of conjugation decreases with each re-use of catalyst, it is necessary to blend the resulting oils. A blended oil containing 25 percent conjugation has been taken as standard, and the success of a series of uses of catalyst is deemed satisfactory if the average conjugation equals or exceeds this figure.

2. Filter Aids Present.- Catalyst activity is also retained in the presence of certain filter aids, if the conditions of subsection 1 are met. For study purposes, the "Celites" and "Super Cels" were selected as representative diatomaceous earths. It was found that those filter aids having pH values of 7.0 or higher were satisfactory under certain conditions, while those having lower pH values were not.

The amount of filter aid present exerts a profound effect on the amount of conjugation obtainable. Likewise, the nature of the filter aid has an important effect. In Table 2.11 are summarized several experiments which illustrate these factors. These experiments were conducted by adding the filter aid to the activated catalyst before the addition of oil. The filter aid was therefore present during both the first and the subsequent uses of the catalyst. It should be noted that if the filter aids were not added until after the first use of catalyst, one more use than the number shown in Table 1.11 would be obtained.

G. Properties of Oil.- The physical properties of representative catalytically conjugated oils are given in Tables 2.1, 2.8, 2.9, and 2.10. Acid numbers do not differ materially, whether the oil results from a first use of catalyst or from a subsequent use.

These oils are outstanding in respect to color, viscosity, and acid numbers. The drying times are substantially less than the nonconjugated oils (Table 2.12), and they compare favorably with drying times for dehydrated castor oil. Other properties of the oils will be indicated in the following discussion on utilization (Part III).

It has not been found possible to standardize the activity of various samples of catalyst to the degree required for the production of oils of uniform properties. For this reason, potential producers of oils using the process described will find it desirable to blend oils containing various amounts of conjugation in order to obtain a uniform product.

H. Recovery of Nickel from Spent Catalysts.- Nickel is readily recovered from spent catalysts for utilization in new catalyst preparations. The first step is extraction of residual oil from spent catalyst. A variety of solvents may be used, including aliphatic and aromatic hydrocarbons, alcohols, chlorinated solvents, and other solvents.

The color of the extracted oil depends on the nature of the solvent used. Thus, Skellysolve F yields a light yellow extracted oil, while chlorinated solvents give a deep red-orange extract, owing to rather complete removal of coloring matter adsorbed during original use of the catalyst. The pale recovered oil may be incorporated into the principal amount of conjugated oil, while a dark extracted oil would be regarded as a byproduct.

The extracted catalyst has pronounced pyrophoric properties. It is therefore treated with dilute nitric acid at once, the mixture finally being

refluxed in order to insure complete removal of nickel. After filtration, the solution of nickel nitrate is concentrated, and the salt is crystallized and recovered. About 90 percent of the original nickel used is recovered by this procedure.

Literature Cited

(1) Kass, J. P., in "Protective and Decorative Coatings," by J. J. Mattiello, John Wiley and Sons, New York, 1944, Vol. IV, pp. 362-405.

III. UTILIZATION OF CONJUGATED OILS

A. Surface Coatings

Preliminary investigations have been conducted on the properties of films from neutral catalytically conjugated oils, and paints, varnishes and alkyd resins derived therefrom. The results obtained should be considered as suggestive only, and not as necessarily representative of the best performance possible.

The set-to-touch time of neutrally conjugated oils varies with the temperature of isomerization, passing through a minimum at about 170° C. (see Table 4.1). Oils used for evaluation were isomerized at 170° C., unless otherwise indicated.

Oil Films

Conjugated soybean and linseed oils were markedly superior to the nonconjugated oils with respect to hot and cold water and alkali resistance. Conjugated soybean oil was superior to nonconjugated linseed oil.

Data are given in Tables 3.1, 3.2, 3.3, and 3.4.

Paints

Paints were compounded in 3 to 4 oz. batches, using a pigment-oil ratio of 3 or 6 to 1. The pigment used was either straight basic carbonate white lead or an 80:20 mixture of this with zinc oxide. Driers were added as napthenates except as otherwise indicated. Single experiments were run with one exception, in which case somewhat discordant results were obtained. Conclusions based on the data presented should therefore be drawn with reservation.

Soybean Oil.- (Tables 3.6 and 3.7) The problem here was elimination of after-tack and the greasy feel characteristic of the dry film. In single coats of paint made with white lead and 5 percent stock drier

(Govt. Spec. No. TT-D-65la, Type I), or made with the 80:20 pigment mixture and lead-manganese driers, after-tack was very slight, but the greasy feel was not eliminated. It was found that a three-coat procedure greatly magnified after-tack. In this case, it was necessary to use the 80:20 mixture of white lead and zinc oxide and to use different driers. Best results were obtained with 0.2 percent zinc and 0.01 percent manganese or with 0.5 percent zinc alone. Under these conditions, after-tack was not objectionable, but the greasy feel was still perceptible. A duplicate preparation with zinc and manganese driers gave, however, a moderately tacky film. Lead and manganese driers were not effective.

Set-to-touch times of the straight white lead paints ranged from 2 to 4 hours and 30 minutes (Sanderson). In the three-coat tests, the third coat set to touch in less time than did the first coat. Set-to-touch times for the first coat varied from 3 hours and 30 minutes to 13 hours and 39 minutes, while the times for the third coat varied from 2 hours and 25 minutes to 7 hours and 45 minutes.

Conjugated soybean oil was always superior to alkali-refined soybean oil with respect to drying time and tack. It appeared equivalent to alkali-refined linseed oil except that it had a greasy feel and did not tend to harden down in the same way as the linseed. Exposure tests now in progress are expected to yield significant information on these points.

Linseed Oil.- Fewer formulations were made with linseed oil. Basic carbonate white lead was used as pigment, and zinc, manganese, lead-manganese, zinc-manganese, and stock driers were used. Except with zinc and zinc-manganese driers, the conjugated oil set to touch much more rapidly than did alkali-refined linseed oil. The films from conjugated oils were less tacky than those from the alkali-refined oil. After-yellowing was substantially lessened, but not absent, in films from conjugated oils. Data are given in Table 3.5.

Paints from both the conjugated soybean and linseed oils brushed easily, but they did not show good flow and leveling properties. It is believed that the poor flow is due to the low acid number of the conjugated oils. Addition of free fatty acid to the oils in preliminary experiments improved flow and leveling; however, the formulations used were not those found later to possess the best drying properties.

Varnishes

A brief study of varnishes prepared from conjugated oils was conducted. Five series of varnishes, using different resins, were prepared according to methods recommended by the resin manufacturers, or according to standard practice (Table 3.9). The varnishes were evaluated for drying rates, hardness, color, cooking speed, and water and alkali resistance. No attempt was made to study variations in drier combinations or cooking procedures.

Owing to the large number of factors which must be considered in developing a varnish from a new oil and in view of the preliminary nature of the present investigation, a detailed report of the tests will not be made. The following general conclusions, which should be considered tentative, may serve as a guide to those interested in this particular application of drying oils. One interested industrial concern which has tested these oils has reported very optimistically upon their results which are at variance with those listed here.

1. The varnishes prepared from dehydrated castor oil were superior in almost every respect to those prepared from the others. This may be due in part to the fact that procedures recommended for preparing dehydrated castor oil varnishes were assumed to be satisfactory for use with conjugated oils in general.
2. Varnishes prepared from conjugated soybean oil were the least satisfactory.
3. Varnishes prepared from conjugated linseed oil and from alkali-refined linseed oil were essentially equivalent. Use of the conjugated oil offers some advantage in speed of cook.
4. Alkali conjugated linseed and soybean oils gave varnishes equivalent to those from neutrally conjugated linseed and soybean oils.

Alkyd Resins

A brief inquiry, similar in scope to that outlined for varnishes, was made into the use of neutrally conjugated oils in alkyd resins. Long, medium, and short oil-length resins were prepared.

In general, the neutrally conjugated oils compared favorably with alkali conjugated oils. The alkali resistance of alkyds from neutrally conjugated soybean oil was outstanding, being equivalent to that of the alkyd from dehydrated castor oil when both alkyds were prepared directly from the oil.

B. Polymerization of Conjugated Oils

The rates of bodying of catalytically conjugated linseed and soybean oils are shown graphically in Graphs 1 and 2. Similar data for nonconjugated linseed and soybean oils and for dehydrated castor oil are also plotted on these graphs. The data for castor oil were taken from the work of Von Mikusch (2) except for those obtained at 590° F. which were determined experimentally. The constants for the various oils used are given in Table 3.10.

The oils were bodied under carbon dioxide at 500°, 560°, and 590° F., the temperature being controlled to ± 1° F. Nonconjugated soybean and linseed oils were studied only at 590° F., owing to the comparative slowness with which they body.

The rates of bodying of the conjugated linseed and soybean oils are substantially more rapid (2 to 5 times) than those of the nonconjugated oils. At 590° F., the rates for dehydrated castor oil and conjugated linseed oil and for conjugated soybean oil and nonconjugated linseed oil are not significantly different. At lower temperatures, however, conjugated linseed and soybean oils are faster bodying than dehydrated castor oil and nonconjugated linseed oil, respectively.

The bodied conjugated linseed and soybean oils are superior to the bodied nonconjugated oils in color, viscosity, bodying loss, and the viscosity obtainable in comparable times. Table 3.11, wherein the properties of the final bodied oils are tabulated, illustrate these facts. While vacuum bodying would be expected to produce light-colored oils of high viscosity and low acid value from the nonconjugated oils, the importance of the properties of the conjugated oils lies in the saving of time and the possibility of use of ordinary kettle bodying equipment. Furthermore, low acid numbers and light colors would be of significance in the cooking of varnishes in open kettles.

In comparison with dehydrated castor oil at 590° F., the decrease in bodying rate obtained with conjugated linseed oil after an initial higher rate is important. This decrease enables oils of very high viscosity to be obtained in a very short time with reduced danger of gelation. The over-all time required with linseed oil, however, is not significantly longer than that required with dehydrated castor oil.

In Table 3.12 and Graph 3 are shown data relevant to the "doubling interval" and the rate of bodying from 2 to 15 poises for the conjugated oils, linseed oil, and linseed pentaerythritol esters. The data for the last oil mentioned are taken from Burrell (1). Doubling intervals were calculated according to the directions of Von Mikusch after correction for bodying incidental to the initial heating-up period.

The mention in this article of firm names or commercial products under proprietary names or names of their manufacturers does not constitute an endorsement by the U. S. Department of Agriculture of such firms or products.

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(2) Von Mikusch, J., Ind. Eng. Chem. 32, 1061 (1940).

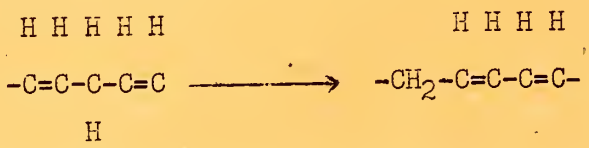
IV. HISTORICAL AND THEORETICAL BACKGROUND

The production of "iso-oleic" acids during partial hydrogenation of unsaturated fat acids and their derivatives is a phenomenon well known to

the hydrogenation industry. The so-called "iso-oleic" acids are known to be mixtures of elaidic acid and other monounsaturated acids wherein the double bond is not in the normal 9-10 position. It has further been established that the production of iso-oleic acids is maximal under conditions of "selective" hydrogenation, that is, when hydrogenation is effected by the agitation process at high temperatures (200° C. or above), low pressures, and in the presence of moderate amounts of catalyst.

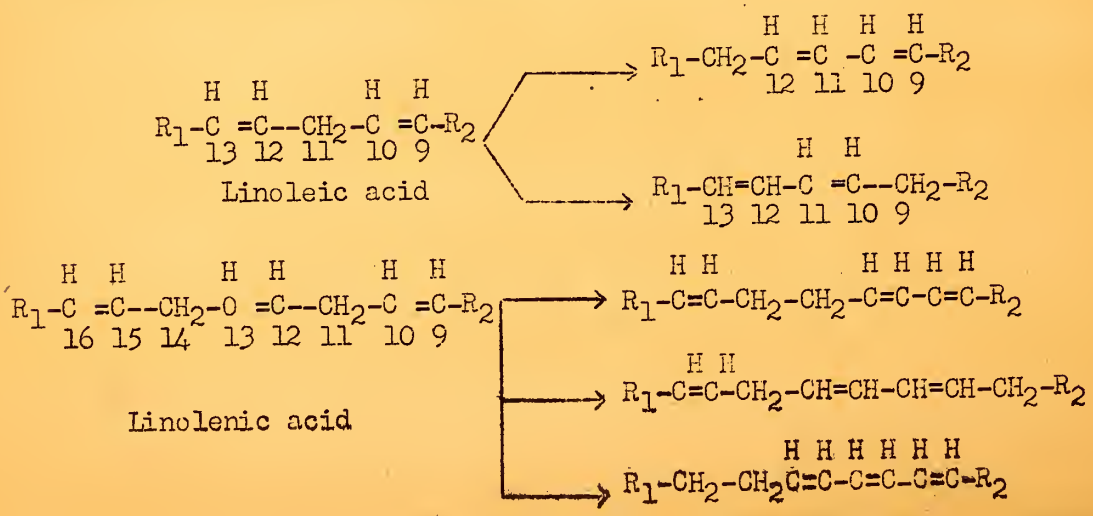
One might therefore expect that under these conditions, but in the absence of hydrogen, hydrogenation catalysts should isomerize linoleic and linolenic acids and their derivatives to conjugated forms. In fact, Waterman and van Tussenbrock (4) and van Dijk (3) observed an increase in refractive index and a fall in iodine number when soybean oil and ethyl linoleate were heated 5 hours in vacuo with nickel catalysts. From similar observations, Waterman and van Vlodrop (5) inferred the production of conjugation in ethyl linoleate. Finally Kass (1) demonstrated by means of the ultraviolet absorption spectra that small amounts of conjugation are actually produced in a variety of oils containing linoleic and linolenic acids when these were heated with catalysts such as nickel, platinum, nickel-on-kieselguhr, decomposed nickel formate, and similar catalysts. The effective catalysts described previously in this report are a development of the original work of Kass.

In the case of alkali conjugation, Kass and Skell (2) postulated that reaction occurred by means of a prototropic shift induced by the alkaline catalyst accompanied by migration of a double bond:



It is probable that neutral catalytic conjugation operates by the same mechanism.

Obviously a number of isomers may be formed, as shown by the following equations, wherein R_1 and R_2 represent the remaining portions of linoleic and linolenic acids in each case:



In the case of linolenic acid, it is noteworthy that molecules containing both double (diene) and triple (triene) conjugation may be formed. Other possible isomers exist for linolenic acid in addition to those shown. To these various position isomers may be added the large number of possible "cis-trans" or geometric isomers. It is apparent that a system of extreme complexity may result from catalytic conjugation of linoleic and linolenic acids or their derivatives. In order to secure a product with the desired properties, it is necessary to control the balance among the various isomers, inasmuch as it is well known that polymerizability and oxidative stability do not necessarily change in parallel fashion from isomer to isomer. With the catalysts described in this report, control of isomer balance is achieved by adjustment of temperature of isomerization.

Table 4.1 clearly indicates the effect of temperature of isomerization on the drying properties of catalytically isomerized oils. It may be noted that the set-to-touch time passes through a minimum at a temperature of isomerization of about 170° C. That the effect is not due simply to varying amounts of conjugation is shown by the data for oils having about the same percent of conjugation (Table 4.2). It is quite possible to produce catalytically an oil containing relatively large amounts of conjugation which will not dry in any reasonable time.

It is noteworthy that existing means of inducing conjugation in linolenic acid result mainly in the formation of isomers containing diene conjugation. To this fact may be attributed in part the failure of these methods to produce an oil having all the properties of tung oil, since the latter contains mainly triene conjugation.

Literature Cited

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Table 2.1.- Properties of typical conjugated oils

Oil	Conjugation			A.V.	Color (Gardner)	Viscosity (Gardner)
	Diene	Triene	Total			
	Percent	Percent	Percent			
Soybean	30.4	2.7	32.1	0.14	4	B-C
Linseed	25.3	8.1	33.4	0.65	3	C-D

- - -

Table 2.2.- Effect of use of catalyst components upon amount of conjugation produced (Soybean oil)

Catalyst	Weight	Time	Temperature	Conjugation
	Percent	Hours	°C.	Percent
Nuchar XXX	15	8	210-20	13
Reduced Nickel 1/	5	4	210-220	nil
Catalyst A (Nuchar XXX)	9	6	170	34
Catalyst A (Nuchar 2A) 2/	9	6	170	34.3
Mixture Nuchar 2A + reduced Ni 3/	12	8	165	8.0

1/ Prepared by reduction of nickel formate.

2/ Sample 1 (see Table 2.3).

3/ Catalyst prepared by reduction of a mechanical mixture of Nuchar 2A (17 g.) and nickel formate (16 g.).

Table 2.3.- Effect of choice of carbon on amount of conjugation (170° C. for 6 hours)

Carbon	Catalyst	Oil	Conjugation
	Type		Percent
Nuchar XXX	D	Soybean	33.0
C-190	D	"	34.0
GL	B	"	27.9
C-115N	B	"	25.8
D	B	"	14.0
2A	B	"	16.9
GFO	A	"	18.4
2 (alkaline)	A	Linseed	12.8
OO oil	A	"	18.5
2 oil	A	"	1.5
OON	A	"	16.0
W	A	"	28.5
2A (1)[1/]	A	"	34.3
2A (2)[1/]	A	"	12.0
WA	A	"	15.5
D	A	"	20.5
Aqua Fan	A	"	2.5
Norite SG II	D	Soybean	[2/]12.2
AG-NC	D	"	[2/] 9.7
A	A	Linseed	nil
Darco G-60	D	Soybean	[3/]10.4

[1/] One sample Nuchar 2A was satisfactory; subsequent samples poor.

[2/] 16 hours at 240° C.

[3/] 10 hours at 260° C.

Table 2.4.- Effect of length of time and temperature of activation on activity of catalyst

Type B catalyst; 7.5 g./100 g. of soybean oil

Time	Temperature	Conjugation
Hours	°C.	Percent
2	310	22.7
1	360	28.3
2	360	34.0
1	450	18.2

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Table 2.5.- Specifications for alkali-refined oils

	Soybean oil	Linseed oil
Spec. gravity	0.924 max.	0.931 max.
Sap. No.	190 min.	190 min.
I.V.	133 min.	185 max.; 175 min.
Acid No.	0.3 max.	0.5 max.
Color	6 max.	5 max.
Viscosity	4 max.	4 max.

Table 2.6.- Effect of catalyst on various grades of oil

Grade of oil (or treatment)	Constants	Catalyst	Conjugation
		Type	Percent
Alkali-refined soybean	See Table 2.5	D	1/ 33 (25)
Crude expeller, soybean	A.V. 1.1	C	10.7
Soybean, alcohol-extracted from beans	---	C	29.0
Alkali-refined soybean 3X alcohol-extracted	---	C	1/ 31.0 (20)
Nonbreak soybean	A.V. 3.5	C	22.5
Degummed soybean (Break: 0.125%)	Color 11; A.V. 0.9	D	30.0
Alkali-refined soybean + free fatty acid	A.V. 0.2	B	33
"	1.5	B	29.9
"	3.0	B	26.6
Alkali-refined soybean heated at 170° C. with 5% Nuchar XXX	---	C	30.0
Alkali-refined linseed	A.V. 0.14; Color 10	D	1/ 29.0 (9.5)
"	A.V. 0.4; Color 4	D	1/ 33 (27)

1/ Value in parentheses for subsequent use of catalyst.

Table 2.7.- Effect upon amount of conjugation produced by varying ratio of nickel to carbon[1/]

Nickel[2/]	Carbon[2/]	Conjugation
Percent	Percent	Percent
1.48	6	32.8
1.54	7	33.4
1.15	6	34.4
2.54	6	26.7
2.11	5	26.8
3.15	5	22.9
1.30	3	13.7
1.94	3	14.3

[1/] Linseed oil used; carbon is Nuchar XXX. Experiments conducted for 6 hours at 165° C., Catalyst Type C.

[2/] Percent based upon weight of oil taken.

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Table 2.8.- Effect of time and temperature of isomerization on amount of conjugation[1/]

Time	Temperature	Conjugation	Color (Gardner)	Viscosity (Gardner)
Hours	°C.	Percent		
		Soybean oil		
6	160	20.3	4	B
6	170	32.1	4	C
4	180	34.9	2	C
4	190	35.7	3	D
		Linseed oil		
6	160	24.7	4	B-C
6	170	28.0	5	C
4	180	32.5	4	C
4	190	33.3	4	E

[1/] Catalyst Type C.

Table 2.9.- Repeated use of catalyst with soybean oil
(6 hours at 170°-175° C.)

Use of catalyst	Oil	Conjugation	Color (Gardner)	Viscosity (Gardner)
	Grams	Percent		
1/	2/			
1	3,480	31.0	---	---
2	3,090	25.1	---	---
3	2,970	27.8	---	---
4	2,818	24.7	---	---
5	2,852	23.5	---	---
6	2,692	27.9	---	---
7	2,602	22.4	---	---
8	2,470	25.9	---	---
9	2,400 (Av. 2,819)	20.4 (Av. 25.4%)	---	---
10	2,330 (Av. 2,770)	18.0 (Av. 24.7%)	---	---
	27,704 Total Wt.			
3/	2/			
1	200	32.0	3	C
2	190	28.0	3	B-C
3	185	28.0	3-4	B-C
4	180	24.0	3-4	B-C
5	175	25.0	4	B-C
6	170	18.0 (Av. 26%)	4	B
4/	2/			
1	200	34.0	4	C-D
2	190	31.0	5	C
3	185	24.5	5-6	B-C
4	180	28.0	5	B
5	175	20.0 (Av. 27.5%)	6	B-C
1/	5/			
1	200	30.0	4	C
2	190	22.0 (Av. 26%)	3-4	B
3	185	18.0 (Av. 23%)	6	B
4	180	13.0 (Av. 21%)	6	A-B

1/ Catalyst D, using Nuchar C-190, unadjusted.
2/ Oil meets specifications of Table 2.5.
3/ Catalyst D, using Nuchar XXX.
4/ Catalyst A, using Nuchar XXX.
5/ Degummed soybean oil (see Table 2.6).

Table 2.10.- Repeated use of catalyst with linseed oil (6 hours at 170° C.)

Use of catalyst	Oil	Conjugation	Color (Gardner)	Viscosity (Gardner)
	Grams	Percent		
1/	2/			
1	200	33	4	D-E
2	190	23	4	B
3	185	26	4	B-C
4	180	27	4-5	B-C
5	175	27 (Av. 27.2%)	4	B-C
3/	2/			
1	200	35	4-5	E
2	190	32	5	C
3	185	26	6	B
4	180	24	6	B
5	175	26 (Av. 28.6%)	6	B-C
1/	4/			
1	200	29.0	5	C
2	190	9.5	6	A-B

1/ Catalyst D, using Nuchar C-190, unadjusted.

2/ Oil meets specifications of Table 2.5.

3/ Catalyst A, using Nuchar XXX.

4/ Oil meets specifications of Table 2.5 except for color, which is 10, not 4.

Table 2.11.- Effect of filter aids on activity of catalyst

Filter aid	pH[1]	Percent[2]	Use of catalyst	Conjugation[3]
"Filter-Cel"	6.3-6.9	7.7	1	32
"	6.3-6.9	7.7	2	18
"	6.3-6.9	7.7	3	18
"Hyflow Super Cel"	7.5-8.5	7.7	1	33
"	7.5-8.5	7.7	2	25
"	7.5-8.5	7.7	3	25
"	7.5-8.5	7.7	4	24
"Celite 503"	7.5-8.5	7.7	1	33
"	7.5-8.5	7.7	2	30
"	7.5-8.5	7.7	3	29
"	7.5-8.5	7.7	4	22
"	7.5-8.5	7.7	5	8
"Celite 501"	7.5-8.5	7.7	1	31
"	7.5-8.5	7.7	2	14
"	7.5-8.5	7.7	3	13
"Hyflow Super Cel"	7.5-8.5	50.0	1	34
"	7.5-8.5	50.0	2	17
"	7.5-8.5	50.0	3	14

1/ Data supplied by manufacturer.

2/ Percent by weight based on activated catalyst.

3/ Soybean oil isomerized 6 hours at 170° C. with Catalyst D using Nuchar C-190.

Table 2.12.- Drying times of various oils

Oil	Drying time[1] with percent drier indicated			
	0.5 Zn	0.2 Pb : 0.01 Mn	0.2 Zn : 0.01 Mn	0.5 Mn
	Hours and minutes			
Alkali-refined soybean	[5] 21:20	[5] 14:55	14:49	12:34
Alkali-refined linseed	13:30	8:40	6:35	6:40
Conj. soybean (2)	Over 70 hrs.	5:20	12:29	5:30
Conj. linseed (3)	18:36	2:00	6:00	4:30
Dehydrated castor (4)	[5] 8:25	[5] 4:00	[5] 5:15	[5] 6:30

1/ Sanderson Drying Machine used.

2/ Contains 29.9 percent conjugation.

3/ Contains 29.5 percent conjugation.

4/ Castung 403.

5/ Some puddling on disc.

Table 2.13.- Repeated use of catalyst with specially degummed soybean oil[1/]

Use of catalyst	Wt. of oil	Total conjugation	Color (Gardner)	Viscosity (Gardner)
	Grams	Percent		
1/1	200	34	4	C
2/2	190	30	3-4	C
3	185	25.5	4	B-C
4	180	24	4	B-C
5	175	23 (Av. 27.3)	4-5	B-C

1/ Temperature 170°-172° C.

2/ Temperature 172°-174° C. for uses 2,3,4, and 5.

- - -

Table 2.14.- Effect of large amounts of catalyst[1/] on production of isomerization in soybean oil

Time	Temperature	Refractive index (n_D^{30})	Conjugation
Minutes	°C.		Percent
0	---	1.4717	---
15	150	1.4732	9
20	165	1.4747	17
25	169	1.4758	23
35	168	1.4770	30
45	168	1.4778	35

1/ Twenty-seven grams of Catalyst D used per 100 g. of oil.

Table 3.1.- Drying Properties of oil films

Oil sample[1]	Kind	Drier	Set-to-touch time[2]	Remarks
1435-36-1	L.O.	5% stock.	1 hr., 30 min.	Not recorded.
1435-36-2	"	"	1 hr., 8 min.	" "
1435-34-1	"	"	1 hr., 15 min.	" "
1435-37-1	"	"	1 hr., 22 min.	" "
1640-26-3	"	0.5% Zn.	18 hr., 36 min.	Slightly difficult sand removal; slight tack.
1640-26-3	"	0.2% Pb-0.01% Mn.	2 hr.	Moderately easy sand removal; light tack.
1640-26-3	"	0.2% Zn-0.01% Mn.	6 hr.	Light tack.
1640-26-3	"	0.05% Mn.	4 hr., 30 min.	Light tack.
Alkali-refined	"	5% stock.	3 hr., 38 min.	Not recorded.
Alkali-refined	"	0.5% Zn.	13 hr., 30 min.	Moderately difficult sand removal; considerable tack.
Alkali-refined	"	0.2% Pb-0.01% Mn.	8 hr., 40 min.	Moderately easy sand removal; considerable tack.
Alkali-refined	"	0.2% Zn-0.01% Mn.	6 hr., 35 min.	Easy sand removal; considerable tack.
Alkali-refined	"	0.05% Mn.	6 hr., 40 min.	"
1644-34-2	S.B.O.	0.5% Zn.	5 hr., 20 min.	Wet after 70 hours.
1644-34-2	"	0.2% Pb-0.01% Mn.	5 hr., 20 min.	Difficult sand removal; light tack.
1644-34-2	"	0.2% Zn-0.01% Mn.	12 hr., 29 min.	"
1644-34-2	"	0.05% Mn.	5 hr., 30 min.	Considerably difficult sand removal; light tack.
Alkali-refined	"	0.5% Zn.	21 hr., 20 min.[3]	Moderately difficult sand removal; light tack.
Alkali-refined	"	0.2% Pb-0.01% Mn.	14 hr., 5 min.	Difficult sand removal; moderate to considerable tack.
Alkali-refined	"	0.2% Zn-0.01% Mn.	14 hr., 49 min.[3]	Difficult sand removal; moderate tack.
Alkali-refined	"	0.05% Mn.	12 hr., 34 min.	Very difficult sand removal; considerable tack.

1/ See Table 3.8.
2/ Determined on Sanderson Meter.
3/ Puddled film.

Table 3.2.- Hot-water tests (100° C.)

Oil sample[1/]	Kind	Drier	Condition after 10-minute exposure	Recovery
1435-36-1	L.O.	5% stock.	(Some melting	Part cleared 10 min.; slight
			(and	dulling.
1435-36-2	"	"	(light	"
1435-34-1	"	"	(cloudiness.	"
1435-37-1	"	"	(	"
Alkali-refined	"	"	Some melting; heavy cloudiness.	Cleared 40 min.; dulled.
1640-26-3	"	0.5% Zn.	Slightly clouded; some melting.	Cleared 10 min.; dulled.
1640-26-3	"	0.2% Pb-0.1% Mn.	No effect.	---
1640-26-3	"	0.2% Zn-0.1% Mn.	Slight cloudiness; some melting.	Cleared 10 min.; dulled.
1640-26-3	"	0.05% Mn.	Light cloudiness; some melting.	Cleared 10 min.; dulled.
1644-34-2	S.B.O.	0.5% Zn.	Very slight cloud; streaked.	Cleared 40 min.; sl. dull.
Alkali-refined	"	0.5% Zn.	Completely melted.	---
1644-34-2	"	0.2% Pb-0.01% Mn.	Very slight cloud.	12 min.; OK.
Alkali-refined	"	0.2% Pb-0.01% Mn.	"	20 min.; OK.
1644-34-2	"	0.2% Zn-0.01% Mn.	"	15 min.; OK.
Alkali-refined	"	0.2% Zn-0.01% Mn.	(Thin film left.)	10 min.; OK.
1644-34-2	"	0.05% Mn.	Very slight cloud; some melting.	Clear 30 min.
Alkali-refined	"	0.05% Mn.	90% melted.	Clear 30 min.; dull.

[1/] See Table 3.8.

Table 3.3.- Cold-water tests (25° C.)

Oil sample[1]	Kind	Drier	Condition after 72 hours' exposure	Recovery
1435-36-1	L.O.	5% stock	(Slight to	OK.; 10 min.
1435-36-2	"	"	(moderate	
1435-34-1	"	"	(cloudiness.	
1435-37-1	"	"	(	
Alkali-refined	"	"	Moderately white.	Clear 13 min.
1640-26-3	"	0.5% Zn.	Slight cloudiness.	Recover 1-1/2 hr.; dulled.
Alkali-refined	"	"	Light cloudiness.	Recover 1 hr. softened; dulled.
1640-26-3	"	0.2% Pb-0.01% Mn.	Very slight cloud.	Recover 1.5 hr.; OK.
Alkali-refined	"	"	50% film gone.	Recover 1 hr.; dulled.
1640-26-3	"	0.2% Zn-0.01% Mn.	Very slight cloud.	Recover 1.5 hr.; OK.
Alkali-refined	"	"	75% film gone.	Recover 1 hr.; dulled.
1640-26-3	"	0.05% Mn.	Slight cloudiness.	Recover 1 hr.; dulled at edges.
Alkali-refined	"	"	30% film gone.	Recover 45 min.; dulled.
1644-34-2	S.B.O.	0.5% Zn.	Light cloudiness.	Recover 15 min.; OK.
Alkali-refined	"	"	75% film gone.	Recover 2-1/4 hr.; OK.
1644-34-2	"	0.2% Pb-0.01% Mn.	Light cloud; slight pitting.	Recover 40 min.; OK.
Alkali-refined	"	"	Heavy cloud.	Sl. cloud after 3 hrs.
1644-34-2	"	0.2% Zn-0.01% Mn.	Moderate cloud; melting.	1 hr. dull.
Alkali-refined	"	"	50% film gone; moderate cloud.	Sl. cloud after 3 hrs.
1644-34-2	"	0.05% Mn.	Moderate cloud; some melting.	1 hr. dull at edges.
Alkali-refined	"	"	Moderate cloud; 25% film gone.	Sl. cloud after 3 hrs.

[1] See Table 3.8.

Table 3.4.- Alkali resistance (0.1N NaOH; 25° C.)

Oil sample[1/]	Kind	Drier	Results
1435-36-1	L.O.	5% stock.	Softened 21 min.; dissolved 18 hrs.
1435-36-2	"	"	Softened 21 min.; dissolved 18 hrs.
1435-34-1	"	"	Softened 22 min.; dissolved 18 hrs.
1435-37-1	"	"	Softened 19 min.; dissolved 18 hrs.
Alkali-refined	"	"	Completely dissolved 1-3/4 hr.
1640-26-3	"	0.5% Zn.	20% off 22 hr.; 100% off 48 hrs.
Alkali-refined	"	"	50% dissolved 15 min.; 100% off 1.5 hr.
1640-26-3	"	0.2% Pb-0.01% Mn.	50% off 22 hrs.; 100% off 48 hrs.
Alkali-refined	"	"	50% off 3 hrs.; 100% off 18 hrs.
1640-26-3	"	0.2% Zn-0.01% Mn.	50% off 22 hrs.; 100% off 48 hrs.
Alkali-refined	"	"	25% dissolved 1.5 hr.; 100% dissolved 3 hrs.
1640-26-3	"	0.05% Mn.	75% dissolved 22 hrs.; 100% off 26 hrs.
Alkali-refined	"	"	50% off 1.5 hr.; 100% off 18 hrs.
1644-34-2	S.B.O.	0.5% Zn.	Cloudy 19 hrs.; 50% off 22 hrs.; 100% off 43 hrs.
Alkali-refined	"	"	Dissolving 12 min.; 75% off 17 hrs.; 100% off 22 hrs.
1644-34-2	"	0.2% Pb-0.01% Mn.	Sl. puckering 19 hrs.; 25% off 22 hrs.; 100% off 138 hrs.
Alkali-refined	"	"	Dissolving 12 min.; 100% off 17 hrs.
1644-34-2	"	0.2% Zn-0.01% Mn.	Cloudy 19 hrs.; dissolving 22 hrs.; 50% off 43 hrs.; 100% dissolved 75 hrs.
Alkali-refined	"	"	Sl. cloud 35 min.; 100% off 17 hrs.
1644-34-2	"	0.05% Mn.	Badly puckered 19 hrs.; softened and loosened 22 hrs.; dissolving 43 hrs.; 10% off 65 hrs.; 100% off 138 hrs.
Alkali-refined	"	0.05% Mn.	Softening 10 min.; loosening 1 hr.; 100% off 17 hrs.

[1/] See Table 3.8.

Table 3.5.- Paints[1] from conjugated linseed oil
(One-coat tests)

Oil sample[2]	Drier	Set-to-touch time[3]	Remarks
1523-29-1	5% stock.	1 hr.	No tack at end of 6 hrs.
1523-15	"	1 hr.	Easy sand removal; very slight tack.
Raw linseed	"	4 hrs.	"
1341-37-2	0.3% Pb-0.03% Mn.	32 min.	Sand removed readily. Trace tack after 4 days.
Alkali-refined	"	5 hrs., 10 min.	Sand removed readily; yellow film; light tack after 66.5 hrs.

1/ Formula: 0.5 oz. oil, 3 oz. basic carbonate white lead; driers as shown.
2/ See Table 3.8.
3/ Determined on Sanderson Meter.

Table 3.6.- Paints[1] from conjugated soybean oil
(One-coat tests)

Oil sample[2]	Drier	Set-to-touch time[3]	Remarks
1523-22-2	5% stock.	2 hrs., 10 min.	Sand removal OK.; not tack free in 44 hrs.
1640-7-2	"	4 hrs., 35 min.	Sand removal easy; very slight after-tack.
1497-37-1	"	2 hrs., 7 min.	Sand removal easy; extremely light after-tack; excellent film.
1497-40-4	"	3 hrs., 15 min.	Sand removal easy; slight after-tack.
1644-21-2	0.3% Pb-0.03% Mn.	2 hrs.	Sand removed easily; light tack.
Alkali-refined	"	9 hrs.	Sand removed with moderate difficulty; extremely tacky.

[1] Formula: 3 oz. oil, 3 oz. basic carbonate white lead; driers as shown..

[2] See Table 3.8.

[3] Determined on Sanderson Meter.

Table 3.7.- Paints[1] from conjugated soybean oil
(Three-coat tests)

Oil sample[2]	Drier	One coat - - - Results - - - Three coats			
		Set-to-touch time[3]	Remarks	Set-to-touch time[3]	Remarks
1644-34-2	0.2% Zn-0.01% Mn.*	6 hrs., 5 min.	Sand removed readily; very slight tack.	3 hrs., 10 min.	Sand removed easily; moderate to considerable tack.
1644-34-2	" *	5 hrs., 40 min.	Sand removed readily; almost free from tack; greasy.	3 hrs., 45 min.	Sand removed readily; slight tack after 66 hrs.
Alkali-refined	" *	9 hrs., 42 min.	Sand removed easily; slight tack.	8 hrs., 50 min.	Moderate to easy sand removal; very tacky.
1644-34-2	0.5% Zn *	13 hrs., 39 min.	Sand removed readily; almost tack free.	5 hrs.	Sand removed readily; light tack.
Alkali-refined	" *	21 hrs., 20 min.	Easy sand removal; slight tack.	13 hrs., 50 min.	Easy sand removal; considerable tack.
1644-34-2	5% stock.	4 hrs.	Moderately easy sand removal; soft film.	7 hrs., 45 min.	Difficult sand removal; moderate tack.
1640-21-2	0.3% Pb-0.03% Mn.	3 hrs., 30 min.	Easy sand removal; light tack.	2 hrs., 25 min.	Moderately difficult sand removal; very tacky.
Alkali-refined	"	9 hrs., 34 min.	Moderately easy sand removal; moderate tack.	25 hrs., 11 min.	Very difficult sand removal; very tacky.
1644-34-2	0.2% Pb-0.01% Mn.	6 hrs., 34 min.	Sand removed readily; light tack.	2 hrs., 50 min.	Sand removed easily; very tacky.

1/ Formula: 1 oz. oil, 3 oz. basic carbonate white lead (except those starred, wherein pigment was 80% basic carbonate white lead and 20% zinc oxide); driers as indicated.

2/ See Table 3.8.

3/ Determined on Sanderson Meter.

Table 3.8.- Identification of oil samples

Sample no.	Description			
	Oil	Catalyst	Temperature of isomerization	Conjugation
			°C.	Percent
1341-37-2	Linseed	A	160	30
1435-34-1	Linseed	C	180	32.5
1435-36-1	Linseed	C	160	24.7
1435-36-2	Linseed	C	170	28.0
1435-37-1	Linseed	C	190	33.3
1497-37-1	Soybean	C	170	32
1497-40-4	Soybean	C (5th use)	170	28.5
1523-15	Linseed	C (16 hrs.)	160	22.3 (pilot plant)
1523-22-2	Soybean	C (3rd use)	200°-170°	26.8
1523-29-1	Linseed	C	170	26.4 (blend 4 runs)
1640-7-2	Soybean	D	160	28
1640-21-2	Soybean	A	160	30
1640-26-3	Linseed	D	170	29.5
1644-21-2	Soybean	D	170	33
1644-34-2	Soybean	D	170 (±1°C.)	29.9

Table 3.9.- Varnish formulation

Resin	Oils used[1]	Oil length	Drier
		Gallon	Percent
Bakelite BR-254	a,b,c,d	30	0.3 Pb; 0.03 Co; 0.02 Mn
Amberol BS/1	a,b,c,d	20	0.3 Pb; 0.03 Co; 0.02 Mn
Arochem 400[2]	a,b,c,d,e,f	25	0.2 Pb; 0.05 Co
Bakelite BR-3360) Ester Gum)[3]	a,b,c,d,e,f	25	0.3 Pb; 0.03 Co; 0.02 Mn
Treated rosin[2,4]	a,b,c,d,e,f	52	0.5 Pb; 0.05 Co

[1] Oils indicated by code letter:
- a. Alkali-refined linseed oil.
- b. Dehydrated castor oil.
- c. Neutral conjugated linseed oil (30.9% conjugation).
- d. Neutral conjugated soybean oil (32.4% conjugation).
- e. Alkali conjugated linseed oil.
- f. Alkali conjugated soybean oil (28.0% conjugation).

[2] Bodied oils used had a viscosity Z, except f which had a viscosity of Y.

[3] Resin: 10% BR-3360, 90% ester gum. Oil: 25% bodied, 75% unbodied.

[4] Rosin treated with 5% CaO and 2% ZnO.

Table 3.10.- Constants of oils used in polymerization study

Oil	Source	Color (Gardner)	Viscosity (poises)	Acid value	Conjugation		
					Diene	Triene	Total
					Percent	Percent	Percent
Soybean	Archer-Daniels Midland Company	5	0.8	0.5	---	---	---
Linseed	Spencer-Kellogg	3	1.0	0.4	---	---	---
Dehydrated castor[1/]	Baker Castor Oil Company (No. 103)	4	2.4	5.5	26.0	0.1	26.1
Conjugated soybean	Northern Regional Research Laboratory	3	1.3	0.5	22.4	6.6	29.0
Conjugated linseed	Northern Regional Research Laboratory	4-5	1.4	0.65	27.7	2.8	30.5

[1/] Used only for data at 590° C.

Table 3.11.- Properties of polymerized oils

Oil	Temperature	Time	Viscosity (poises)	Color (Gardner)	Acid value	Bodying time
	°F.	Min.				
Soybean	590	315	4.1	1-2	10.3	---
	590	900	60.0	7-8	25 0	---
Conjugated soybean	500	530	3.3	2	1.3	---
	560	475	32.3	4	5.4	---
	590	315	58.4	4	7.4	---
Linseed	590	180	12.4	1	8.0	4.1
	590	600	459.0	7	20.1	---
Conjugated linseed	500	345	15.4	4	1.35	---
	560	210	119.0	4	2.80	1.3
	590	180	728.0	5	5.50	1.4
Dehydrated castor	500	360	1/ 5	---	---	---
	560	210	1/ 82	---	---	---
	590	130	1,014	4-5	---	---

1/ Data of Von Mikusch, loc. cit.

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Table 3.12.- Doubling intervals (temperature range 560°-590° F. viscosity increase 2-15 poises)

Oil	Doubling interval
	°F.
Conjugated linseed	13.5
Linseed pentaerythritol esters	20.0
Linseed	23.0
Dehydrated castor	27.5
Conjugated soybean	35.0

Table 4.1.- Effect of temperature of isomerization on the drying times of conjugated oils and paints[1/]

Oil	Temp. of isomerization	Set-to-touch time[2/] of	
		Oil film	Paint
	°C.	Hours	Hours
Alkali-refined soybean	---	11 hrs., 30 min.	10 hrs.
	160	5 hrs., 30 min.	6 hrs.
	170	4 hrs., 15 min.	4 hrs.
	180	5 hrs.	5 hrs., 30 min.
	190	> 5 hrs.	5 hrs., 30 min.
Alkali-refined linseed	---	4 hrs.	6 hrs., 30 min.
	160	2 hrs., 15 min.	3 hrs., 15 min.
	170	1 hr., 30 min.	2 hrs., 45 min.
	180	1 hr., 30 min.	3 hrs.
	190	2 hrs., 30 min.	3 hrs., 30 min.

1/ Paints contained 25 percent oil and 75 percent basic carbonate white lead. Both oils and paints contained 5 percent stock drier (Pb, Mn).

2/ Determined on Sanderson Meter.

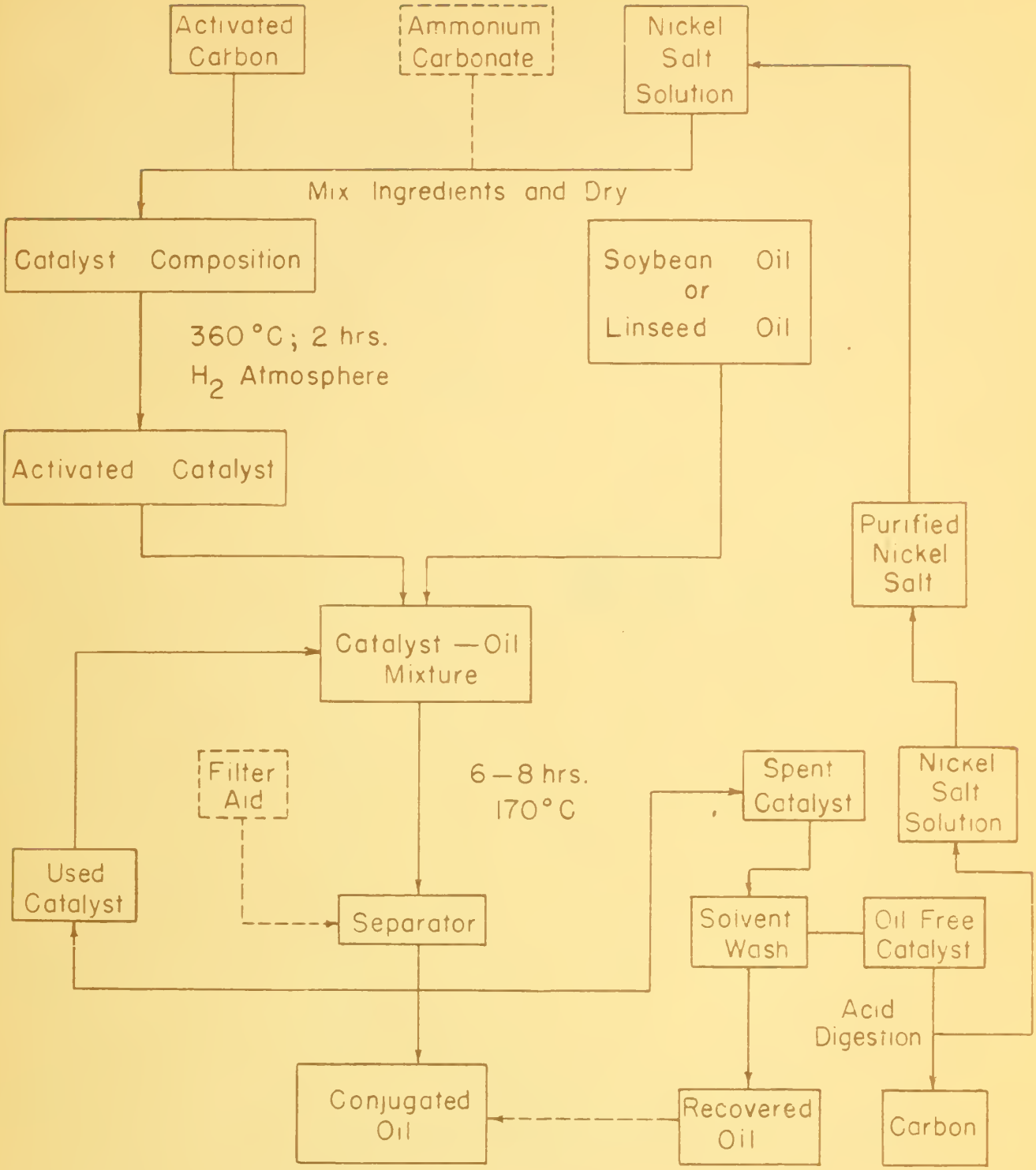
Table 4.2.- Effect of temperature of isomerization on drying properties of conjugated oils

Oil	Temperature of isomerization	Conjugation	Set-to-touch time[1]	Remarks
	°C.	Percent	Hours	
Linseed[2]	170	29.5	2 hrs.	Light tack.
Linseed[2]	210	28.3	2 hrs. to 2 hrs., 30 min.	Very tacky after 48 hrs.
Soybean[3]	160	28.0	4 hrs., 30 min.	Very slight after-tack.
Soybean[3]	1 hr., 200°; 5 hrs. 170°	26.8	2 hrs.	Not tack free in 44 hrs.

[1] Determined on Sanderson Meter.

[2] Drier: 0.2% Pb; 0.01% Mn.

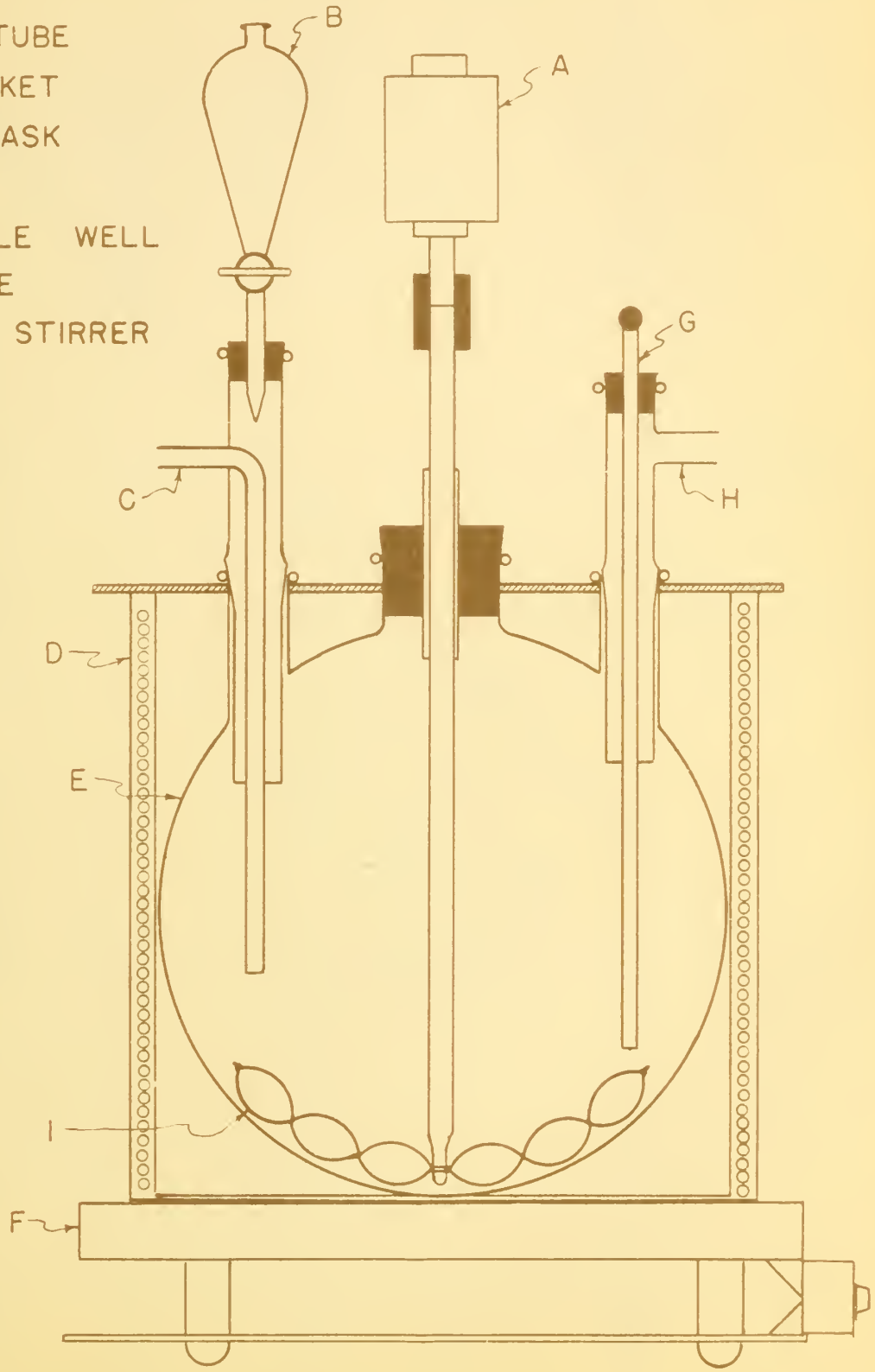
[3] Paint: 1 oz. oil; 2 oz. basic carbonate white lead; 5% stock drier.



NEUTRAL CATALYTIC ISOMERIZATION FLOWSHEET

OP-L-519-P

A. VARIABLE SPEED MOTOR
B. FUNNEL
C. GAS INLET TUBE
D. HEATING JACKET
E. 5-LITER FLASK
F. HOT PLATE
G. THERMOCOUPLE WELL
H. OUTLET TUBE
I. HERSHBERG STIRRER



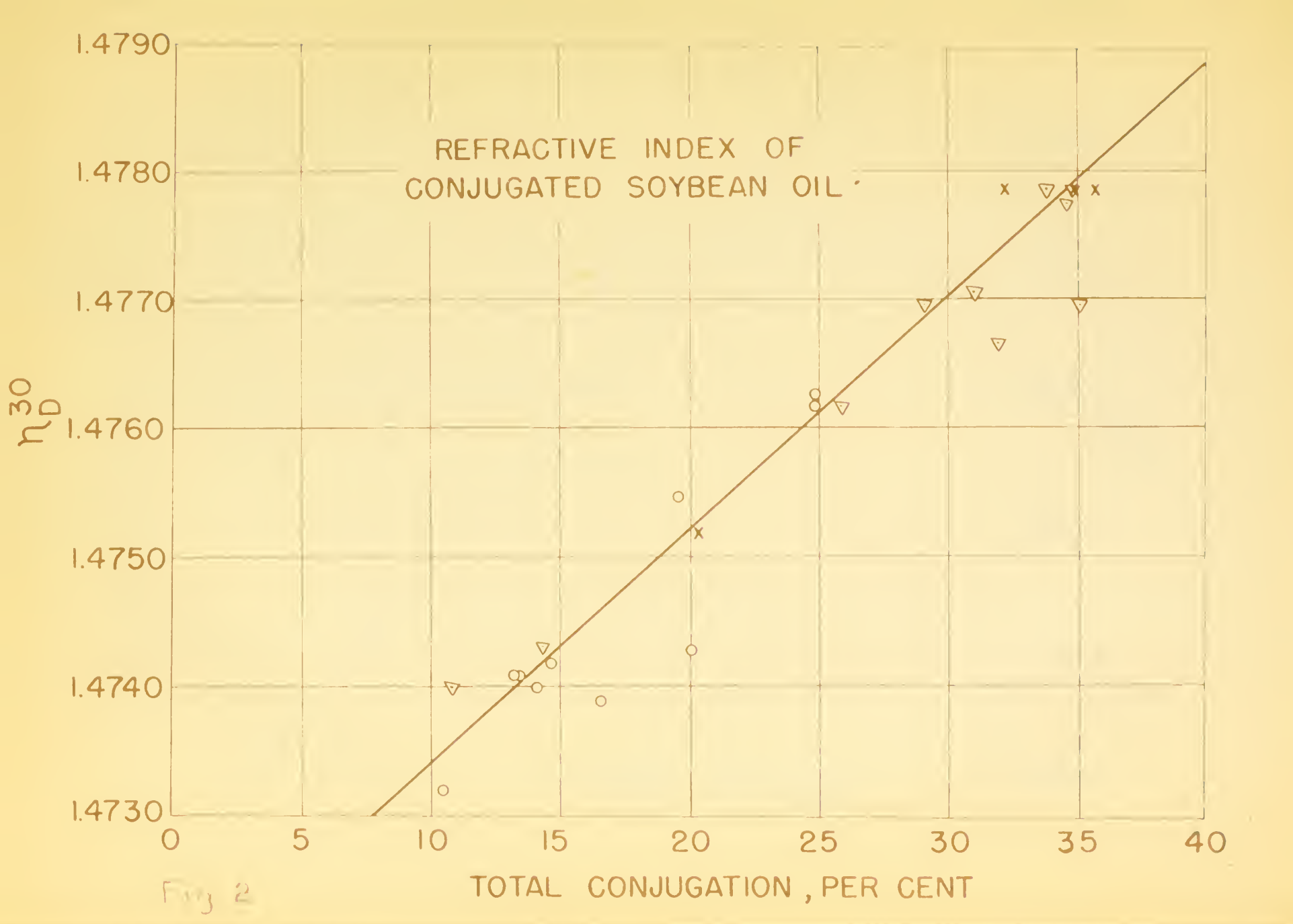

REFRACTIVE INDEX OF
CONJUGATED SOYBEAN OIL
n_D^{30}
1.4790
1.4780
1.4770
1.4760
1.4750
1.4740
1.4730
0
5
10
15
20
25
30
35
40
TOTAL CONJUGATION, PER CENT

Fig 2

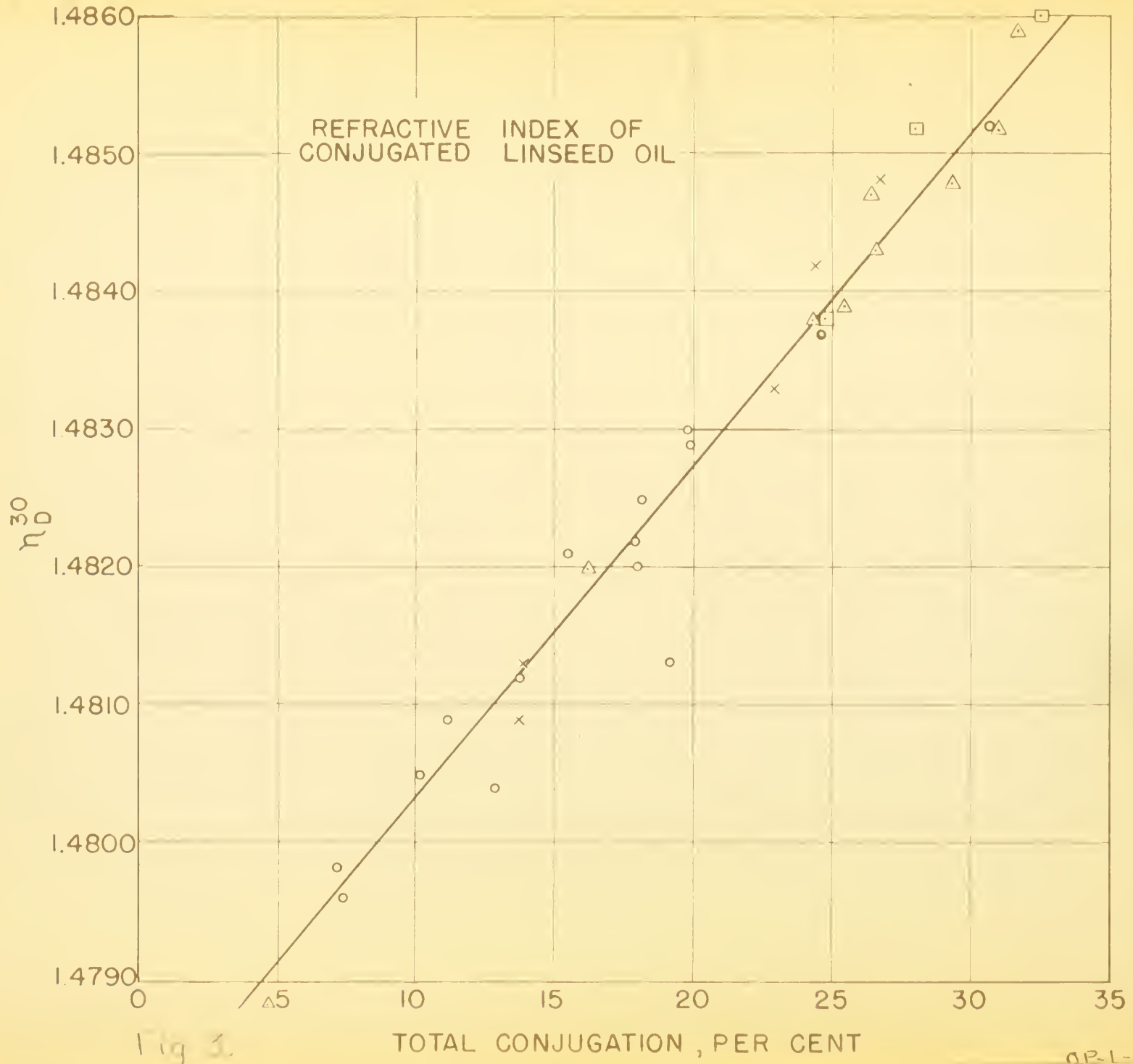


Fig 3.

OP-1-380-P-3

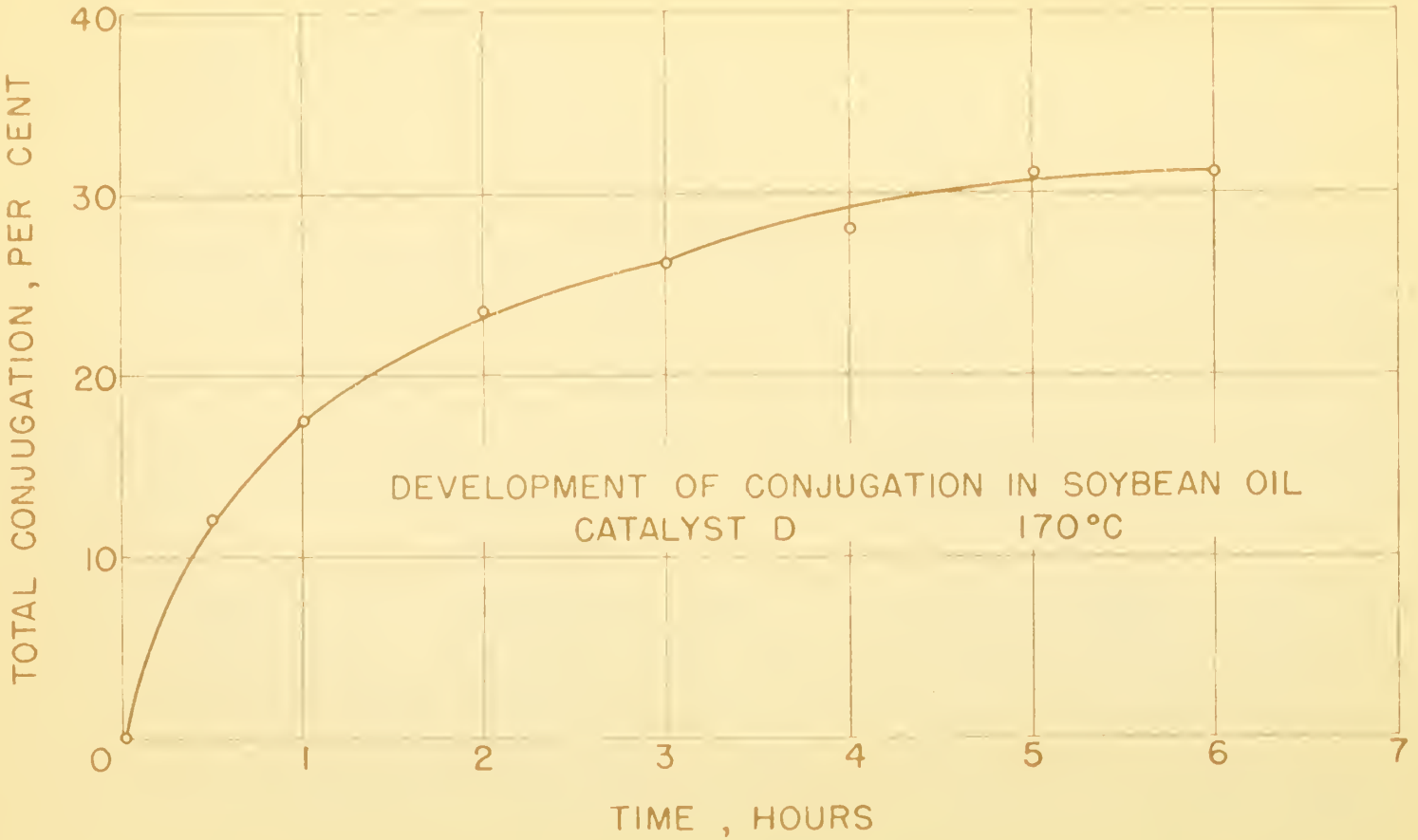
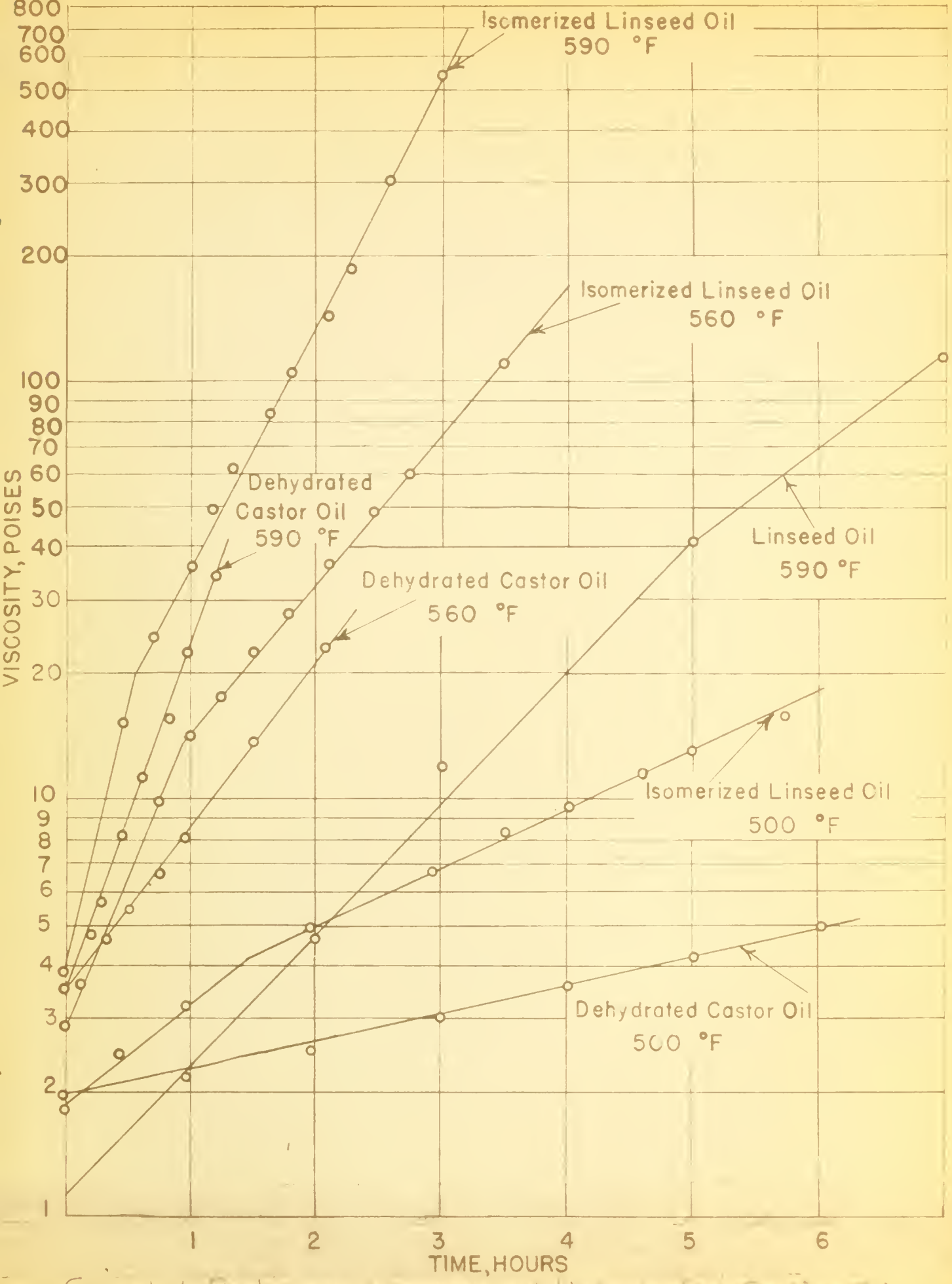
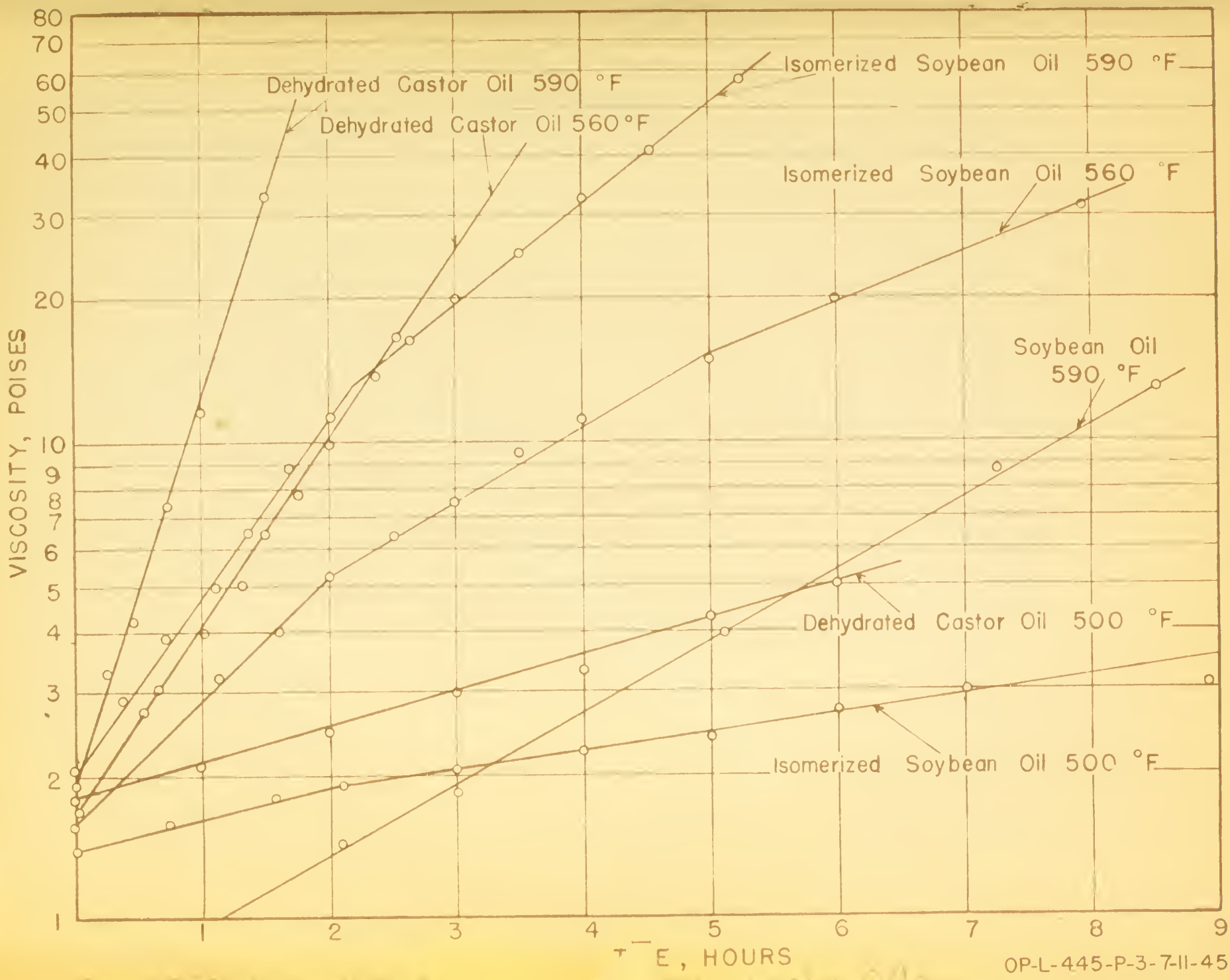

TOTAL CONJUGATION, PER CENT
40
30
20
10
0
1
2
3
4
5
6
7
TIME, HOURS
DEVELOPMENT OF CONJUGATION IN SOYBEAN OIL
CATALYST D
170°C

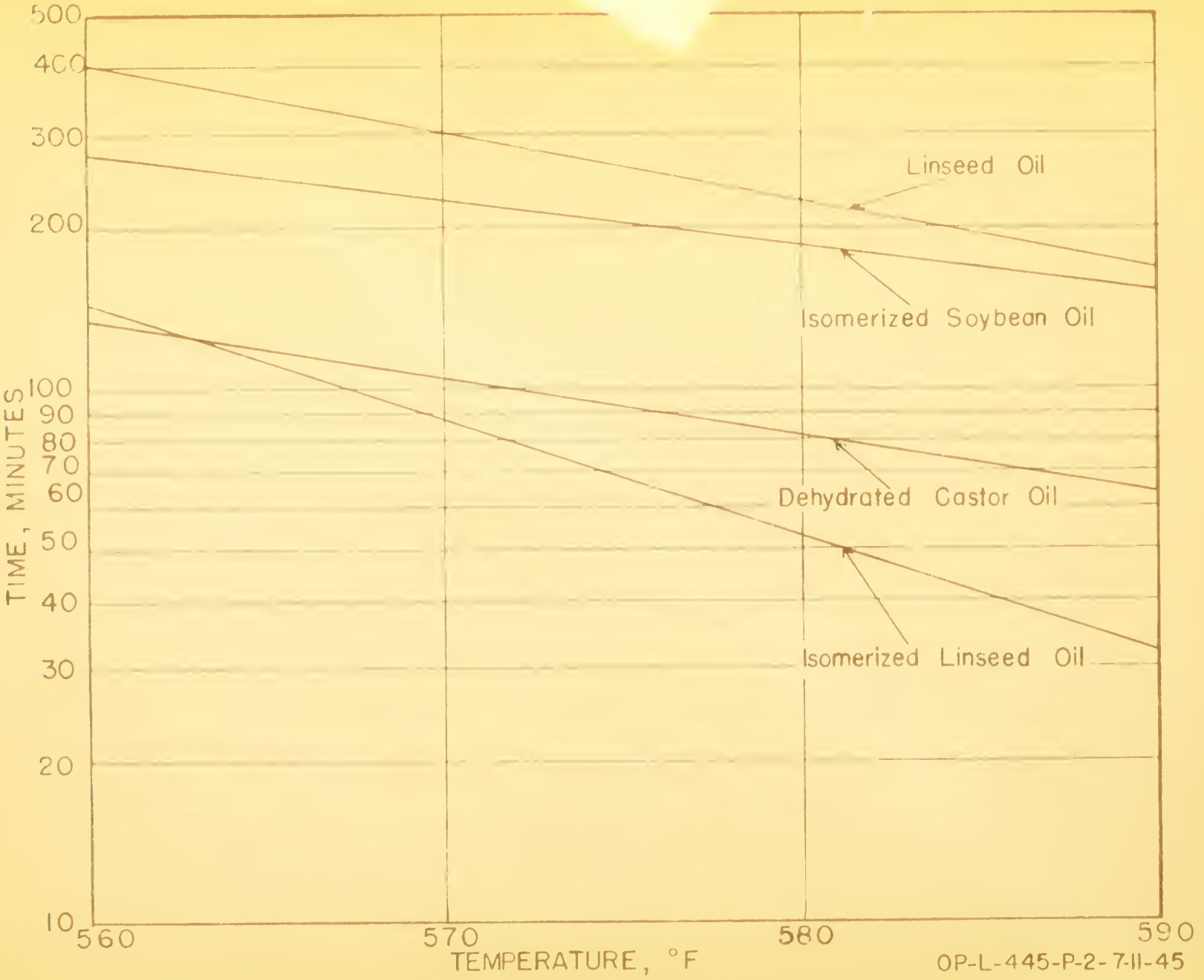
Fig. 3



OP-L-445-P-1 - 7-11-45

Graph 1- Bodying of Linseed and Dehydrated Castor Oils


Dehydrated Castor Oil 590 °F
Dehydrated Castor Oil 560 °F
Isomerized Soybean Oil 590 °F
Isomerized Soybean Oil 560 °F
Soybean Oil 590 °F
Dehydrated Castor Oil 500 °F
Isomerized Soybean Oil 500 °F
VISCOSITY, POISES
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
1
2
3
4
5
6
7
8
9
E, HOURS
OP-L-445-P-3-7-11-45


500
400
300
200
100
90
80
70
60
50
40
30
20
10
TIME, MINUTES
560
570
580
590
TEMPERATURE, °F
Linseed Oil
Isomerized Soybean Oil
Dehydrated Castor Oil
Isomerized Linseed Oil
OP-L-445-P-2-7-11-45